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Summary for Period

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X-RAY STUDIES OF SIMPLE HYDROGEN-BONDED CRYSTALS WITH FREEZING POINTS BELOW ROOM TEMPERATURE

I. THE CRYSTAL STRUCTURE OF FORMIC ACID

II. THE CRYSTAL STRUCTURE OF ISOCYANIC ACID

by

Gene B. Carpenter, Director
and
Werner C. von Dohlen

Metcalf Research Laboratory
Brown University
Providence, Rhode Island

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I. THE CRYSTAL STRUCTURE OF FORMIC ACID

ABSTRACT

A partial study of the crystal structure of formic acid has been made. The structure determination will not be continued because similar work has been completed by Holtzberg, Post, and Fankuchen. The results of the present investigation are in agreement with their results.

1. INTRODUCTION

At the beginning of this work, formic acid was one of the simple substances whose crystal structures had not been investigated. It was an attractive substance for study for several reasons: it would supply more data on the length of bonds in carboxylic acids; it would provide more data on the nature of hydrogen bonds; and it might provide an explanation for the unusually large dielectric constant which has been observed for the crystal(1). It had the additional

(1) J.F. Johnson and R.H. Cole, J. Am. Chem. Soc., 73, 4536 (1951)

practical advantage that the apparatus necessary to freeze and preserve crystals of formic acid need not be very elaborate since it freezes only a few degrees below room temperature.

2. EXPERIMENTS

It was necessary to construct apparatus for growing and maintaining crystals inside a conventional X-ray diffraction camera. The work of Abrahams, et al.(2) had shown that a smooth stream of

(2) S.C. Abrahams, R.L. Collin, W.N. Lipscomb, and T.B. Reed, Rev. Sci. Instr., 21, 396 (1950)

cold gas blowing over the capillary containing the liquid sample accomplishes this. In our arrangement, tank nitrogen was passed through a copper coil immersed in a cooling bath and then through a

Dewar-jacketed glass delivery tube, so that a stream of cold nitrogen was directed vertically downward onto the sample. The coil was soldered through the bottom of an insulated metal can and was joined to the delivery tube by means of a Housekeeper seal. The can was filled with a Dry Ice-isopropanol mixture. Temperatures of about -30°C. could be maintained at the sample with a reasonable rate of flow of nitrogen. The entire assembly was mounted directly above the camera on a metal tripod. The sample was mounted in a sealed capillary of about 0.5 mm internal diameter on a Unicam oscillation-rotation X-ray goniometer.

In order to grow a single crystal of formic acid, the sample was cooled slowly by gradually increasing the flow of cold nitrogen. Usually a few relatively large crystals would form in the capillary, which could then be adjusted to bring a single crystal into the X-ray beam. It was also possible to obtain single crystals by freezing the sample quickly, then remelting most of it with a jet of warm air, and finally allowing the remaining crystals to grow slowly by gradually removing the air jet. In our experience formic acid crystals grew always with the same crystallographic direction parallel to the axis of the capillary.

After a suitable crystal had been grown, the film was wrapped around a cylindrical frame replacing the film-holder provided with the instrument. A split cylinder of brass was then placed around the film to hold it in place and to contain the X-rays.

All experiments used Ni-filtered CuKα X-radiation from a Philips Diffraction Unit.

Rotation photographs and 15° oscillation photographs, about the axis labelled $\underline{c}$, were prepared from several crystals at -15°C.

3. RESULTS

From measurement of the layer line spacing on the best rotation photograph the length of the c-axis was found to be 5.4 Å. The $\ell = 0$ layer of the reciprocal lattice was reconstructed by a straightforward graphical procedure. From this reconstruction, the lengths a = 10.3 and b = 3.64 Å were determined. The crystal is orthorhombic. Systematic absences indicated (h0ℓ) present only with h = 2n and (0kℓ) present only with $k + \ell = 2n$, where n is an integer. These results were somewhat tentative because of the relatively small number of reflections observed. They indicate that the space group is probably $Pna2_1$ or Pnam.

At this point the similar work of Holtzberg, Post, and Fankuchen (3), on the structure of formic acid, came to our attention. Since our preliminary results were in agreement with theirs, it seemed pointless to continue our work on formic acid. The axial lengths reported here are all slightly larger than those obtained by Holtzberg, et al. This is explained partly by the fact that our photographs were prepared at -15° while theirs were prepared at -45°, but mostly by the fact that our values have not been refined as thoroughly as theirs.

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(3) F. Holtzberg, B. Post, and I. Fankuchen, J. Chem. Phys., 20, 198 (1952)

II. THE CRYSTAL STRUCTURE OF ISOCYANIC ACID

ABSTRACT

Isocyanic acid is orthorhombic, with space group Pnma or $Pn2_1a$. The unit cell dimensions are a = 10.72 ±0.06, b = 5.15 ±0.03, and c = 3.56 ±0.03 Å. There are 4 molecules in the unit cell.

1. INTRODUCTION

The structure, in the vapor, of the compound of empirical formula CHON has been shown to be that represented by the structural formula HNCO, according to electron diffraction[1], microwave[2],

(1) E.H. Eyster, R.H. Gillette, and L.O. Brockway, J. Am. Chem. Soc., 62, 3236 (1940)

(2) L.H. Jones, J.N. Shoolery, R.G. Shulman, and D.M. Yost, J. Chem. Phys., 18, 990 (1950)

and infrared[3] investigations. In the crystal the molecular structure appears[3] to be the same, but the structure HOCN may be possible. It should be possible, from an X-ray structure determination, to decide if the second alternative is realized in the crystal.

(3) G. Herzberg, Discussions Faraday Soc., No. 9, 92 (1950)

The hydrogen bond pattern in the crystal should be informative as to the configuration favored by hydrogen bond formation, because such bonds should be the strongest intermolecular attractions in the crystal and because the hydrogen atom is not collinear with the rest of the molecule. An accurate determination of the structure should provide significant information about bond lengths and angles and about the general considerations which determine the mode of packing of molecules in the crystal.

2. EXPERIMENTS

Isocyanic acid was prepared by the method of Linhard[4], as

(4) M. Linhard, Z. anorg. u. allgem. Chem., 236, 200 (1938)

modified by Herzberg[3], by the depolymerization of the trimer, cyanuric acid. Eastman cyanuric acid was dried under vacuum at 200°. It was sublimed at 450° in a Pyrex tube and the vapor was swept through a 12 inch long Vycor tube, maintained at 700°, by a stream of dry nitrogen under reduced pressure. The resulting isocyanic acid vapor was then condensed in a trap cooled with a Dry Ice-isopropanol bath. This trap contained finely divided silver oxide to oxidize any HCN formed by the pyrolysis.

The product was then distilled from this trap into a second one containing P_2O_5 to remove moisture. This distillation was effected under reduced pressure and at a temperature from -50° to -40°. The isocyanic acid was allowed to stand in contact with the desiccant for several hours at about -80°. It was then distilled similarly into a device for filling capillaries. By this stage, the product was a clear colorless liquid which froze to a white solid.

Several capillaries were then filled with the product by means of a filling device which allowed a controlled amount of liquid to be transferred from a reservoir to a capillary by a controlled positive pressure of dry nitrogen. The thin-walled capillaries, of 0.7 to 0.5 mm outside diameter were then sealed off under vacuum while the sample was kept frozen under the surface of liquid nitrogen. The capillaries were preserved in a Dry Ice-isopropanol bath until used in order to prevent the repolymerization which becomes appreciable when the temperature rises above -20°.

The purity of the product was then roughly checked by measuring the vapor pressure, at several temperatures, with a mercury manometer. The values differed from those given by Linhard[4] by less than 5%.

A new apparatus for freezing the sample in the X-ray camera was constructed, like that of Abrahams, et al.[5]. It consisted of a

(5) S.C. Abrahams, R.L. Collin, W.N. Lipscomb, and T.B. Reed, Rev. Sci. Instr., 21, 396 (1950)

4-1/2 liter Dewar flask reservoir for liquid nitrogen and a Dewar-jacketed delivery tube bent so that a stream of cold nitrogen was directed vertically downward onto the sample. The reservoir contained an electrical heating coil to control the rate of boiling of the nitrogen and hence the temperature at the sample. The delivery tube had an internal diameter of about 13 mm. Frosting of the sample capillary was minimized by shaping the delivery tube so that the gas jet was fairly wide and non-turbulent. In addition, a room air-conditioner reduced the moisture in the air. Temperatures down to -150° were maintained by this apparatus. At -125°, liquid nitrogen was consumed at the rate of 2 liters/hour.

The X-ray unit, the camera, and the film-holder were those described in part I.

Several powder photographs of isocyanic acid were prepared, both for comparison with similar photographs of cyanuric acid as a further check against polymerization and for increased accuracy of certain measurements.

Several single crystals were grown by partial melting of a polycrystalline sample, by means of a small electric heating coil, followed by slow refreezing (5). Isocyanic acid crystals grew always with the c axis parallel to the axis of the capillary.

Single crystal rotation and 15°-oscillation photographs were then prepared at -130 ±5°. Ni-filtered CuKα radiation was used except for one rotation photograph which was prepared with Zr-filtered MoKα radiation; the latter showed no reflections beyond those recorded on the CuKα photographs because of the relatively rapid decline of intensity with scattering angle. One set of oscillations was recorded on packs of three films for use in intensity estimation.

3. RESULTS

The ℓ = 0 and 1 layers of the reciprocal lattice were reconstructed graphically from oscillation photographs; they indicated that the crystal is orthorhombic. The rotation photographs were then indexed, in part, by means of this reconstruction, and the separations of zero layer indexed reflections were measured. The a and b lengths were determined from a least squares treatment of 24 such measurements. The c length was determined approximately from the layer line spacing and was refined by measurements of indexed arcs on powder photographs. The resulting unit cell dimensions are

$$a = 10.72 \pm 0.06 \text{ Å}.$$

$$b = 5.15 \pm 0.03$$

$$c = 3.56 \pm 0.03$$

Systematic absences indicated the following: hk0 present only with h even, 0kℓ present only with k + ℓ even. The probable space groups are then Pnma and $Pn2_1a$.

If 4 molecules per unit cell is assumed, the density should be 1.45g/cm^3. The density of solid isocyanic acid has not yet been measured; however the density of cyanuric acid is 1.77g/cm^3 and the polymerization is accompanied by a contraction. It is therefore unlikely that there be other than 4 molecules per cell.

The determination of the atomic arrangement is being continued.